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TIME-RESOLVED RAMAN SPECTRUM OF SHOCK-COMPRESSED DIAMOND

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ABSTRACT

A method has been developed for time-resolved Raman measurements under shock loading to examine the first order Raman line of diamond ($\omega_0 = 1333$ cm^{-1}). The diamond samples were subjected to uniaxial strain along the [110] direction to a longitudinal stress of 121 kbar. The observed spectral changes are consistent with frequency shifts calculated according to a phenomenological model used to describe stress effects on the zone center phonons of cubic materials.

The use of spectroscopic measurements in shock wave experiments has increased considerably in recent years.[1-8] These measurements compliment the continuum data obtained from wave profile measurements[9] and have the potential to provide an understanding of shock compressed materials at the atomic/molecular level. The paper by Moore and Schmidt[10] provides a comprehensive review of the different types of spectroscopic measurements under shock loading, including a good discussion of the experimental requirements. Because of the nature of shock wave studies, both the performance and interpretation of these experiments are difficult. In order to develop a detailed understanding of the time-dependent physical and chemical phenomena of interest in shock compression experiments, it is desirable to obtain time-resolved optical measurements and to correlate these with time-resolved continuum data (stress and/or particle velocity). Examples of time resolved spectroscopy under shock loading may be seen in the absorption work[7] on liquid CS_2 and the luminescence measurements in ruby crystals.[8] Because these measurements probe the electronic states of the shocked sample, it is difficult to establish a unique relationship between the observed spectral changes and the atomic/molecular deformation. The present work was motivated by a need to develop complementary methods for examining time-dependent structural changes at the atomic/molecular level in shocked crystals. Raman spectroscopy is well suited for this purpose.

Here, we report on a method for obtaining time-resolved spontaneous Raman spectra in shocked diamond. Diamond was selected because of its large Raman cross-section,[11] high mechanical strength,[12] the considerable body of static high-

pressure measurements,[13–17] and the potential for development of a high-stress optical transducer for shock wave studies. In the present experiments, the frequency shift of the first-order Raman line at $\omega_0 = 1333$ cm^{-1} was observed under uniaxial strain along the [110] crystallographic direction. This line is triply degenerate, at ambient conditions, with a linewidth[18] of 1.65 cm^{-1} at 300K; the frequency shift and/or splitting have been examined under static high pressure[13–15] and under uniaxial stress loading[16] along the [100] and [111] directions. Hydrostatic pressure shifts, $\Delta\omega_H$, ranging from 0.28 to 0.36 cm^{-1}/kbar have been reported.[13–15]

The experimental layout is shown in Figure 1. Light from a flash-pumped dye laser (Candela SLL 500, 514.5 nm, 500 ns pulse length, 10 mJ pulse energy) was delivered to the target chamber by mirrors, and was focused in the diamond to a spot diameter of approximately 1 mm. The incident angle at the back sapphire disk was about 20 degrees. Scattered light was collected in the backward direction along the sample axis and focused into a double spectrograph (Spex 1680, 1200 groove/mm gratings). The Raman spectrum was then dispersed over time by an image converter streak camera (Hadland Imacon 790). The streak image was intensified by a gated microchannel plate image intensifier (ITT F4113 P11) and reduced in size by a tapered fiberoptic bundle (Galileo Electro-Optics 3:1 reduction). Finally, the image was digitally recorded by an optical multichannel analyzer (EG&G 1460 OMA with model 1254 Vidicon detector). A time-resolved spectrum recorded by this apparatus consists of 50-100 spectra recorded sequentially at 30-15 ns intervals.

Details of the sample construction are also indicated in Figure 1. The type IIa diamonds (Doubledee Corporation) were obtained in the form of disks approximately 0.3 mm thick and 4.0 mm in diameter, and were oriented such that the [110] crystallographic axis was normal to the disk surface. The diamond was placed between two z-cut sapphire disks (Union Carbide Corporation) in a brass cell for mounting in the shock facility. A thin brass washer (<0.2 mm) was used to center the diamond in the cell during assembly. Sapphire was chosen as a window and impactor material because of its high mechanical impedance and well characterized shock properties.[19]

Shock waves were produced by impacting the sample assembly with a projectile fired from a single-stage, compressed gas gun.[20] Details related to spectroscopic measurements in impact experiments are presented in the work by Horn and Gupta.[8] The sapphire impactor, shown in Figure 1, is mounted on an aluminum plate which was bonded to the end of the projectile. On impact, a stress wave is launched into the front sapphire window and propagates to the diamond, leaving the material behind it in a state of uniaxial strain along the propagation direction. The stress achieved is determined by the impact velocity and by the mechanical impedance of the impactor and sample. The stress obtained in the diamond varies over time in a somewhat complex way because of reflections which occur at the sapphire/diamond interfaces. The uniaxial strain condition persists in the central region of the sample until the arrival of rarefactions from the sample edges; edge effects occurred in these experiments approximately 100 ns after the shock first entered the diamond.

At the stresses of interest in the present experiments, the diamond[21] can be modeled as a linear elastic solid and the sapphire[19] as a nonlinear elastic solid. The stress-particle velocity (σ - u) relation can be expressed as:

$$\sigma = \rho_0 \mathrm{D} \mathrm{u}$$

where ρ_0(diamond) = 3.512 g/cc and ρ_0(sapphire) = 3.985 g/cc. The wave velocities are given by:

$$\mathrm{D}(\text{diamond}^{21} \text{ along } [110]) = 18.33 \text{ mm}/\mu\text{s}$$
$$\mathrm{D}(\text{c}-\text{axis sapphire}^{19}) = 11.19 + 1.0\text{u mm}/\mu\text{s}$$

As indicated in previous studies,[8] the shock measurements along the c-axis in sapphire are in excellent agreement with calculations based on the higher order constants given by Hankley and Schuele.[22]

The layered configuration shown in Figure 1 results in a stress history in the diamond as shown in Figure 2. After two transit times through the diamond, the longitudinal stress in the diamond is very nearly equal to the stress produced on impact in the front sapphire window. Because of the time-resolution of our optical detection system, we could not observe the reverberation, seen in Figure 2, in the optical measurements. The arrival of rarefactions from the sample edges in the observation region, as previously discussed, limits the useful duration of the optical observations to only a few tracks on the OMA. In future experiments we plan to use thinner samples and faster time-resolution. For further discussion of shock wave phenomena, we refer the reader to the articles by Gupta,[23] and by Davison and Graham.[24]

Two experiments were performed, both at an equilibrated longitudinal stress of 121 kbar. This stress value ensured that the rear window was always within the elastic limit of the sapphire, and permits a straightforward analysis of these preliminary experiments. The Raman spectra at ambient conditions and at 121 kbar for one experiment are shown in Figure 3. Uniaxial strain along the [110] direction is expected to completely remove the three-fold degeneracy of the Raman line, as discussed below; however, the spectral resolution of these experiments was not sufficient to observe the splitting. As indicated above, the transit time of the shock wave through the diamond is approximately 16 *ns* (*of the same order* as the experimental time resolution) and the effect of the initial 143 kbar stress was also not resolved. The frequency shift at 121 kbar of the observed peak, determined from spectra taken over the 100 *ns* period following the initial entry of the shock wave into the diamond, was found to be $(8.9 \pm 1.0)\text{cm}^{-1}$. A preliminary comparison between the measured and expected values is presented below.

The strain-induced changes in frequency of zone-center phonons in diamond may be calculated according to the formulation of Anastassakis et. al.[25] This is a phenomenological approach in which the two atoms in the diamond unit cell are assumed to obey the equation of motion

$$m\frac{\partial^2 u_i}{\partial t^2} = -\left[\sum_j K_{ij} u_j \delta_{ij} + \sum_{klm} \frac{\partial K_{ik}}{\partial \eta_{lm}} \eta_{lm} u_k\right] \qquad (2)$$

where u_i is the i^{th} component of the relative displacement, m is the reduced mass, and the K_{ij} are atomic force constants satisfying cubic symmetry. With the

assumption of a harmonic solution, equation 2 results in a secular equation with eigenvalues, λ, relating the ambient $\left(\omega_0 = \sqrt{K_{11}/m}\right)$ and strained-crystal phonon frequencies as $\lambda=\omega^2-\omega_0^2$. Because the strain derivatives are evaluated in the unstrained condition, they are also constrained by the cubic symmetry.

For a uniaxial strain, η, along [110], the strains in the crystallographic system are given by $\eta_{xx} = \eta_{yy} = \eta_{xy} = \eta/2$, and the eigenvalues are $\lambda=\eta(p+q\pm 2r)/2$ and ηq, where p, q, and r correspond to the three independent strain derivatives allowed by cubic symmetry. The displacement eigenvectors $[u_x, u_y, u_z]$ are [1, 1, 0], [1, -1, 0] and [0, 0, 1] respectively. The p, q, and r parameters are given by Grimsditch et. al.[16] as $p = -2.92\omega_0^2$, $q = -1.90\omega_0^2$, and $r = -1.20\omega_0^2$ from measurements of the diamond Raman line under uniaxial stress. Insertion of these values yields $\lambda = -3.6\eta\omega_0^2$, $-1.2\eta\omega_0^2$, $-1.9\eta\omega_0^2$ (note that η is negative in compression). We then see that the largest frequency shift occurs for the mode in which displacement occurs along the strain direction, and that the three-fold degeneracy is entirely removed.

For the 121 kbar longitudinal stress, we find $\eta = -0.010$. Hence, the expected frequency shifts are $\Delta\omega = 23.8\ cm^{-1}$, $8.0\ cm^{-1}$, and $12.6\ cm^{-1}$. These values are indicated in Figure 3. As stated earlier, the splitting of these lines is not resolved in our experiments. The results in Figure 3 show that the calculated shifts are comparable to our measurements but better data are needed for quantitative comparisons.

In summary, an experimental method has been developed and applied to obtain time-resolved Raman measurements in shocked solids. The data obtained

are reasonable and demonstrate the feasibility of the method. It is apparent, however, that improved spectral and temporal resolution is needed to use this method for analyzing time varying deformations. Because of the large stiffness of the diamond, high stress experiments are desirable. Experimental improvements are currently underway and it is expected that time-resolved Raman measurements will play an important role in understanding shock deformation in solids.

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Figure Captions

1. Schematic view of the experimental system. Light from a flash-pumped dye laser is incident on the diamond sample at an angle of approximately 20 degrees. Raman scattered light is focused into a double spectrograph (DS). The spectrum is dispersed over time by an electronic streak camera (SC), and the streak image is digitally recorded by an optical multichannel analyzer (OMA). The remaining component designations in the figure refer to the microchannel plate intensifier (MCP), fiberoptic reducer (FR), Vidicon detector (V), and the trigger/delay generator (T/D). A charged pin shorted by the projectile body produces a trigger signal, which is then delayed appropriately for firing the laser and triggering the recording system.

2. Calculated stress-time history for a point in the center of the diamond sample. The longitudinal stresses in the diamond and sapphire come to equilibrium within two transits of the waves reflected from the diamond-sapphire interfaces.

3. Diamond Raman spectrum at ambient conditions and at 121 kbar longitudinal stress (uniaxial strain along [110]). The splitting of the triply degenerate line under stress is not resolved.

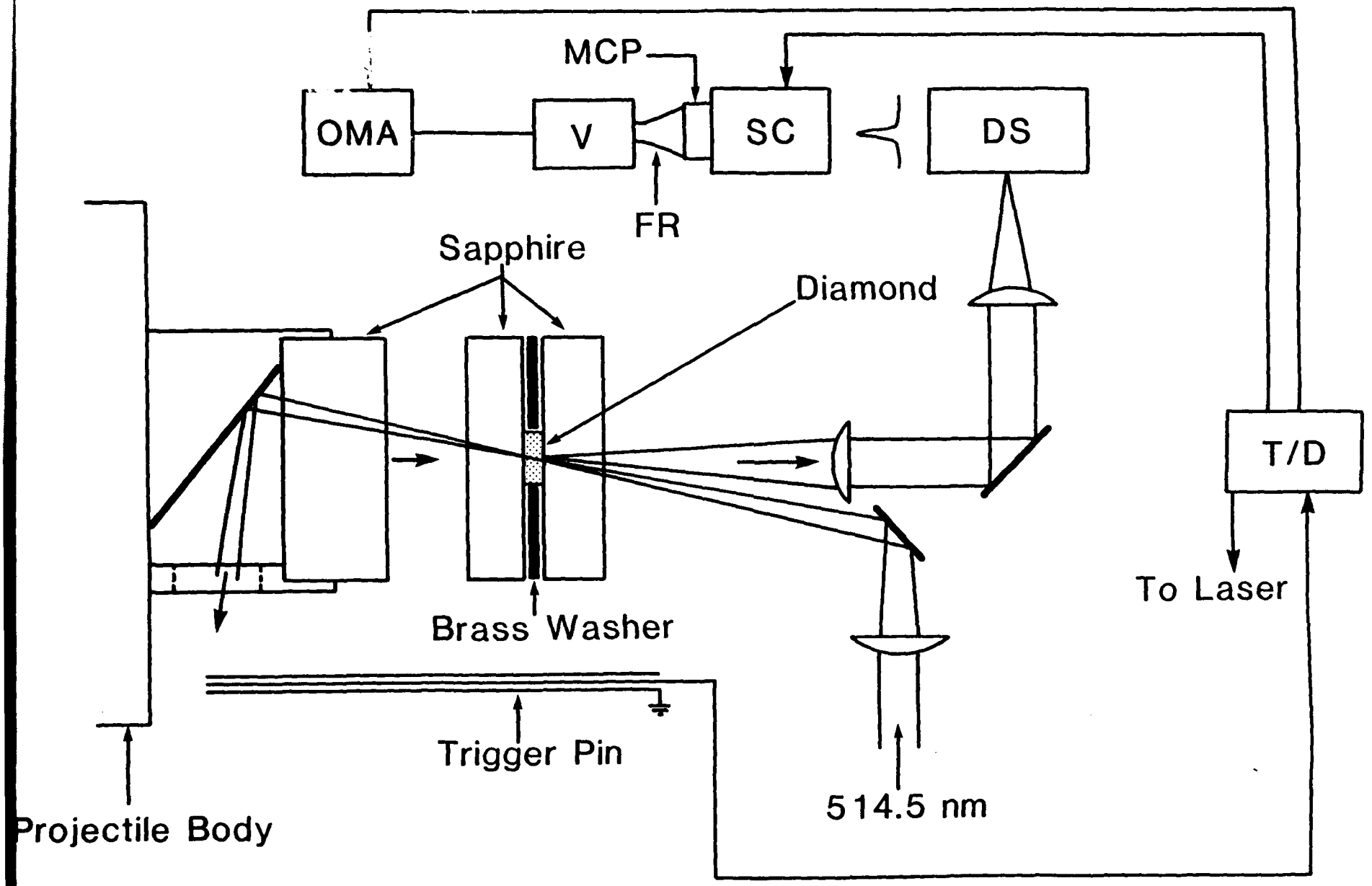
MCP
OMA
V
SC
DS
FR
Sapphire
Diamond
T/D
To Laser
Brass Washer
Trigger Pin
514.5 nm
Projectile Body

Figure 1

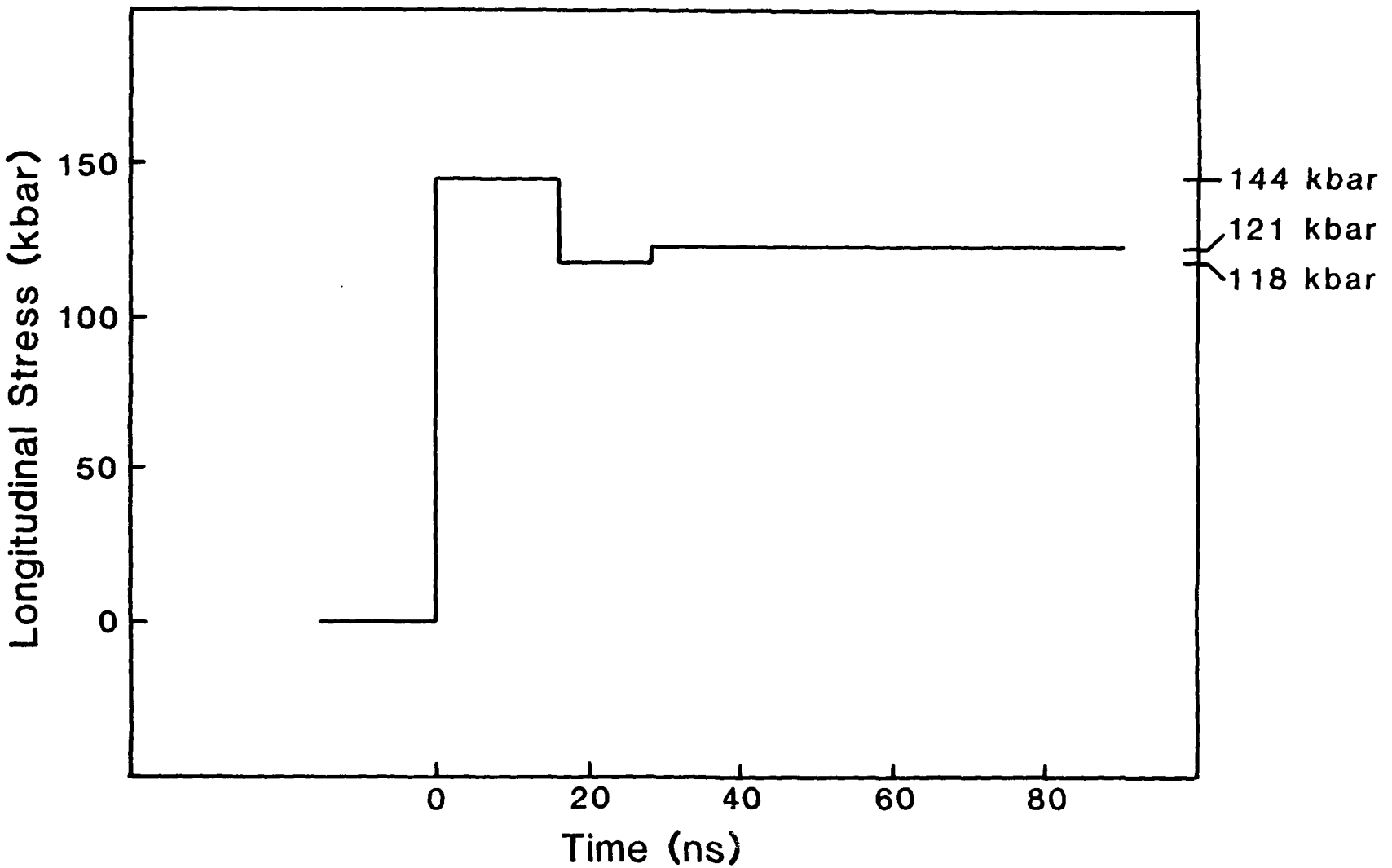
Longitudinal Stress (kbar)
150
100
50
0
144 kbar
121 kbar
118 kbar
0
20
40
60
80
Time (ns)

Figure 2

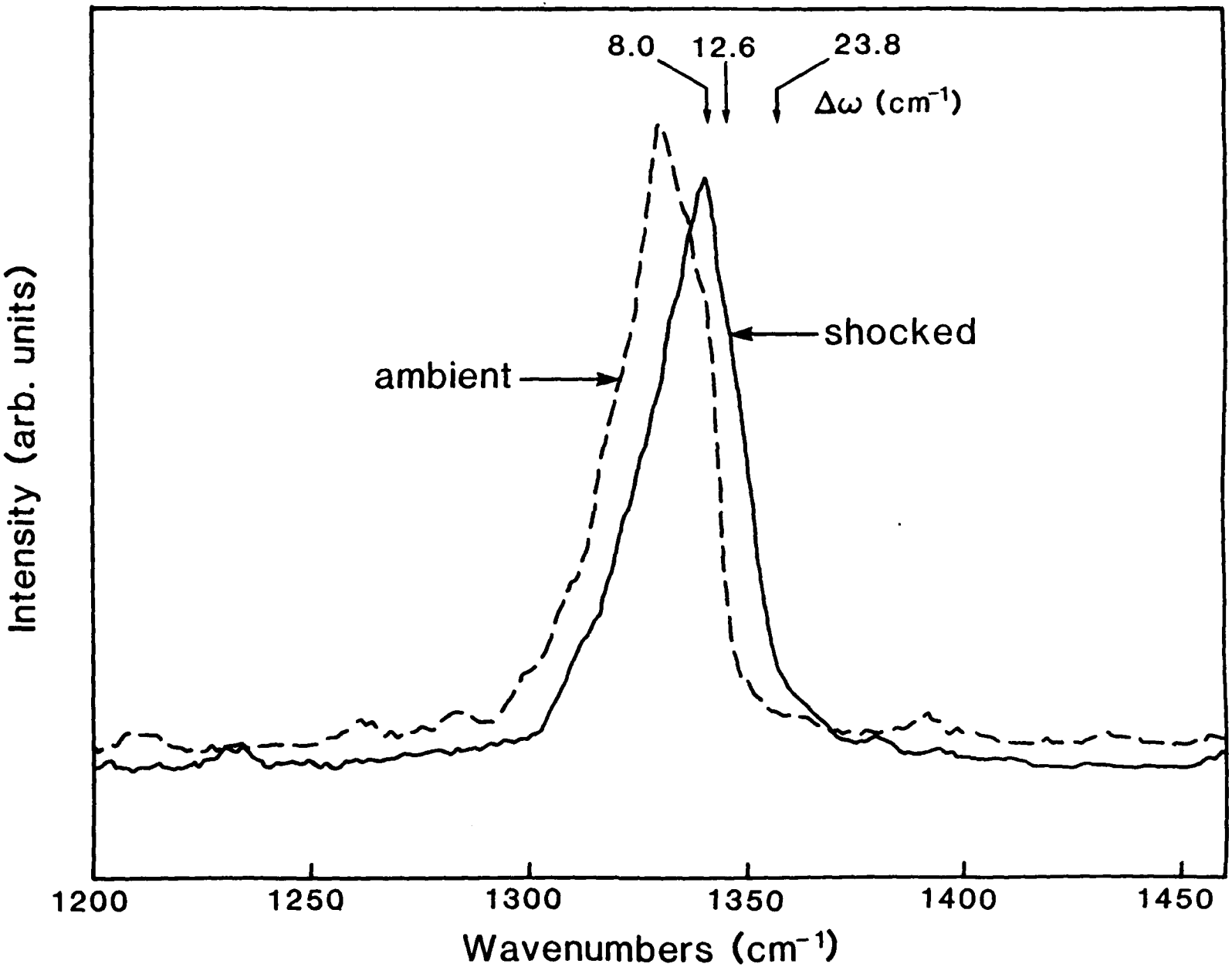
8.0
12.6
23.8
Δω (cm⁻¹)
shocked
ambient
Intensity (arb. units)
1200
1250
1300
1350
1400
1450
Wavenumbers (cm⁻¹)

Figure 3